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Preparation of Poly(phosphoric acid piperazine) and Its Application as an Effective Flame Retardant for Epoxy Resin

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Abstract A phosphorus-nitrogen containing flame retardant additive of poly(phosphoric acid piperazine), defined as PPAP, was synthesized by the salt-forming reaction between anhydrous piperazine and phosphoric acid, and the dehydration polymerization under heating in nitrogen atmosphere. Its chemical structure was well characterized by Fourier transform infrared (FTIR) spectroscopy, ^{13}C and ^{31}P solid-state nuclear magnetic resonance measurements. The synthesized PPAP and curing agent *m*-phenylenediamine were blended into epoxy resin (EP) to prepare flame retardant EP thermosets. The effects of PPAP on the fire retardancy and thermal degradation behavior of cured EP/PPAP composites were investigated by limiting oxygen index (LOI), vertical burning (UL-94), thermogravimetric analysis/infrared spectrometry (TG-IR) and cone calorimeter tests. The morphologies and chemical compositions of char residues for cured epoxy resin were investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The results demonstrated that the flame retardant EP thermosets successfully passed UL-94 V-0 flammability rating and the LOI value was as high as 30.8% when incorporating 5wt% PPAP into the EP thermosets. The TGA results indicated that the synthesized PPAP flame retardant additive possessed high thermal stability and excellent charring capability. Meanwhile, the incorporation of PPAP stimulated the epoxy resin matrix to decompose and charring ahead of time due to its catalytic decomposition effect, which led to a higher char yield at high temperature. The morphological structures and the analysis results of XPS for char residues of EP thermosets revealed that the introduction of PPAP benefited the formation of a sufficient, more compact and homogeneous char layer containing phosphorus-nitrogen flame retardant elements on the material surface during combustion. The formed char layer with high quality effectively prevented the heat transmission and diffusion, limited the production of combustible gases, and inhibited the emission of smoke, leading to the reduction of heat and smoke release.

Keywords Synthesis; Poly(phosphoric acid piperazine); Flame retardant; Epoxy resin thermosets; Thermal degradation

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INTRODUCTION

Epoxy resins (EPs) are widely used in electronics, electrical, chemical corrosion, mechanical manufacturing, aerospace and many other industries due to the excellent adhesion, corrosion resistance, electrical insulation and high strength properties[1–3]. However, a high-quality flame retardant grade is required because the fire risk is a major drawback of epoxy resin thermosets[4]. Consequently, the improvement of flame retardant property of epoxy resin thermosets has become an urgent project and attracted much attention in recent years[5].

Traditionally, halogenated compounds have been widely used as co-monomers or additives for epoxy resins to endow them with flame retardancy. However, the flame retardant epoxy resins with halogen elements release the corrosive and toxic gas and black smoke during the combustion process, which are extremely harmful to the environment and human health[6, 7]. In this context, the development and application of halogen-free flame retardants has become a subject of extensive investigation for epoxy resins. Up to now, a wide variety of halogen-free flame retardants have been proposed to improve the flame retardancy including phosphorus[8–12], boron[13–16], silicon[17–20], nitrogen[21–23] and so on. Among them, the usage of phosphorus-containing compounds is a prospective way to improve the flame retardancy of epoxy resins because the flame retardants can stimulate epoxy resins to form a carbonaceous char, which isolates heat transmission and suppresses the release of combustible gas and smoke in condensed phase[24, 25]. Moreover, the compounds can enter into the vapor phase by a radical mechanism to interrupt the exothermic processes and suppress combustion. In this case, PO, P and P_2 species are likely to react with H and OH radicals to form HPO[26, 27]. Although the phosphorus-containing flame retardants exert flame retardant effect both in gaseous and condensed phases, the flame retardant performance is not effectively enhanced when organophosphorus flame retardants are used alone, which

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cannot meet the increasing stringent requirement for flame retardant grade. Recently, many efforts have been made to explore more efficient synergistic flame retardant systems containing two or more flame retardant elements for epoxy resins. The previous research demonstrated that the flame retardant efficiency could be obviously enhanced when phosphorus and nitrogen existed simultaneously in the epoxy resin systems[28–31]. In our previous work[32], the polymeric flame retardant additive of polymelamine tetramethylene phosphonium sulfate (PMTMPS) was synthesized and incorporated into EP thermosets; the samples passed UL-94 V-0 flammability rating when the loading amount of PMTMPS was 11 wt%, which indicated that the flame retardant efficiency of PMTMPS for EP was relatively low and required to be further improved. Generally, the flame retardant additives with high phosphorus content may benefit the formation of sufficient and compact char layer. In the condensed phase, the formed char layer is critical for the enhancement of flame retardancy of materials. The compound of piperazine is widely used as the raw materials for preparing the efficient flame retardant due to its excellent char-forming ability[33–35]. We aim to prepare a polymeric flame retardant additive with piperazine structure and high phosphorus content, and use it as a flame retardant additive for preparing epoxy resin thermosets with superior flame retardant performance.

Herein, we report the synthesis of a phosphorus-nitrogen containing flame retardant additive of poly(phosphoric acid piperazine) derived from the salt-forming reaction between piperazine and phosphoric acid and the dehydration polymerization. The synthesized compound was then incorporated with epoxy resin to prepare flame retardant EP thermosets. The flame retardant properties, thermal degradation behavior, combustion behavior and flame retardant mechanism of the EP thermosets were characterized and disclosed.

EXPERIMENTAL

Materials

Epoxy resin (diglycidyl ether of bisphenol-A (DGEBA), E-44, epoxide equivalent weights = 213 g/epoxide) of technical grade was supplied by Xingchen Synthetic Material Co. Ltd. (Nantong, China). *m*-Phenylenediamine (PDA) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Anhydrous piperazine was purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Phosphoric acid was supplied by Tianli Chemical Reagent Co. Ltd. (Tianjin, China).

Synthesis of Poly(phosphoric acid piperazine)

The synthetic route of flame retardant additive poly(phosphoric acid piperazine) (PPAP) is shown in Scheme 1. A 250 mL five-necked flask was equipped with a thermometer, a mechanical stirrer, a nitrogen inlet, a pressure-equalizing funnel and a reflux condenser. Phosphoric acid (115.3 g, 85 wt%) was added at room temperature. Piperazine (43.1 g) was dissolved in 150 mL of distilled water and then the solution was added dropwise into the flask at 40 °C over 30 min in nitrogen atmosphere under stirring. The mixture was gradually heated to 85 °C and maintained at that temperature for another 2 h. Then the reaction mixture was cooled to room temperature and filtered. The obtained white crystals were washed with cold distilled water three times, and dried at 105 °C in a vacuum oven for 2 h to a constant weight. White solid of piperazine diphosphate (133.2 g) was obtained. The obtained intermediate of piperazine diphosphate was put into the tube furnace at 230 °C for 40 min in nitrogen atmosphere with a flow rate of 20 mL·min^{-1}. The condensation polymerization of the intermediate was carried out by the dehydration reaction between piperazine diphosphate. Finally, the target compound was obtained as a white powder (121.5 g, yield 92.1%).

Preparation of Cured Epoxy Resin

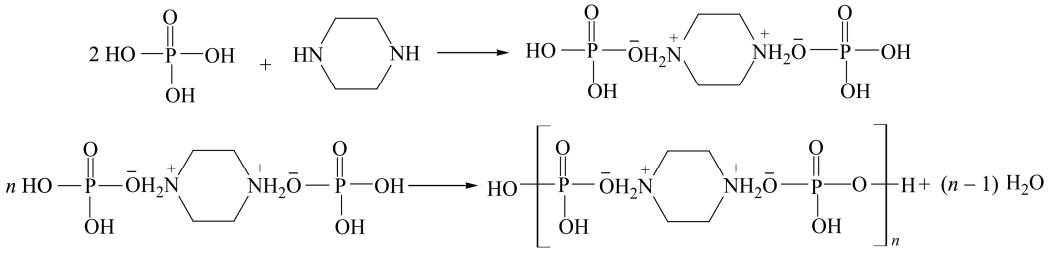
In order to prepare the flame retardant epoxy resin thermosets with different contents of flame retardant additive, PPAP, epoxy resin and the curing agent (PDA) were mixed homogeneously by a mechanical stirrer at 90 °C with an equivalent ratio of epoxide/N-H = 1/1. The liquid mixture was poured into a mold, cured at 105 °C for 1 h and post cured at 150 °C for 2 h. After curing, the samples were cooled to room temperature for carrying out the related tests. The contents of PPAP flame retardant additive in epoxy resin thermosets are listed in Table 1.

Chemical Structure Characterization

The chemical structure of synthesized poly(phosphoric acid piperazine) was determined by solid-state nuclear magnetic resonance (NMR) measurement and Fourier transform infrared (FTIR) spectroscopy. ^{13}C and ^{31}P solid-state NMR measurements were recorded on the plus 400 NMR spectrometer operating at 400 MHz. FTIR spectra were recorded (the samples pressed into slices with KBr powder) using a Nicolet Avator 360 spectrometer.

Flame Retardancy Test

The limiting oxygen index (LOI) values were measured at room temperature by a JF-3 oxygen index meter (Jiangning Analysis Instrument Company, China) according to ISO



Scheme 1 Synthetic route to poly(phosphoric acid piperazine)

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Table 1 Formulations and flame retardancy for cured epoxy resin composites

Sample	Components (wt%)		Flame retardancy		
	EP	PPAP	LOI (%)	UL-94	Dripping
EP-0	100	0	21.1 ± 0.1	No rating	No
EP-1	99	1	28.6 ± 0.2	No rating	No
EP-2	98	2	29.5 ± 0.1	No rating	No
EP-3	97	3	29.9 ± 0.1	No rating	No
EP-4	96	4	30.4 ± 0.2	V-1	No
EP-5	95	5	30.8 ± 0.2	V-0	No
EP-6	94	6	31.3 ± 0.1	V-0	No

4589-2: 2006 standard with specimen dimension of 130 mm × 6.5 mm × 3 mm. Vertical burning (UL-94) tests were performed on a CZF-2-type instrument (Jiangning Analysis Instrument Company, China) according to ANSI/UL 94-2013 test standard with specimen dimension of 130 mm × 13 mm × 3.2 mm. UL-94 testing results were evaluated by burning ratings V-0, V-1, or V-2. V-0 rating corresponds to the best flame retardancy of polymeric materials.

Mechanical Properties Test

Tests of tensile strength and flexural strength of all the samples were performed by Regeer computer controlled mechanical instrument (Shenzhen, China) and Notched Izod impact instrument (Chengde, China), respectively, according to the ASTM D256 standards. The dimensions of samples were 150 mm × 10 mm × 4 mm. At least five specimens were tested for each sample and the average values are reported.

Cone Calorimeter Test

The combustion behavior under ventilated condition was measured using cone calorimeter (West Sussex, UK), in conformance with ISO 5660-1 standard. Samples with size of 100 mm × 100 mm × 4 mm were exposed to a cone at a heat flux of 50 $kW \cdot m^{-2}$. For each sample, three specimens were tested to ensure significant and reproducible data. The average values and their standard deviations are reported.

Thermogravimetric Analysis/Infrared Spectrometry (TG-IR)

TG-IR of the samples was performed on the TGA Q5000 IR thermogravimetric analyzer interfaced to the Nicolet 6700 FTIR spectrophotometer. FTIR was directly connected to TG and measured the gaseous decomposition products from TG by real time. About 4–5 mg of sample was put in an alumina crucible and heated from 50 °C to 800 °C at a heating rate of 10 $K \cdot min^{-1}$ under nitrogen atmosphere with a flow rate of 20 $mL \cdot min^{-1}$.

Scanning Electron Microscopy (SEM)

SEM was used to examine the morphology of char residue obtained from the cone calorimeter tests using a FEI QuanTa-200 (Eindhoven, Netherlands) SEM. The accelerating voltage was set to 15 kV. The surface of char residues was sputter-coated with gold layer before examination.

X-ray Photoelectron Spectroscopy (XPS)

XPS measurement was carried out in an ultrahigh vacuum system equipped with a Kα hemispherical electron analyzer (Thermofisher Scientific Company), using a monochromated Al Kα source, at a base pressure of 1.0×10^{-4} Pa. C, N, P, O and Al elements were analyzed.

RESULTS AND DISCUSSION

Characterization of PPAP

The chemical structure of synthesized PPAP was characterized by FTIR, ^{13}C and ^{31}P solid-state NMR measurements, respectively. Figure 1 presents the FTIR spectrum of PPAP. The absorption peak at 989 cm^{-1} is corresponding to O—H bending variation in P—OH groups, the peak at 1101 cm^{-1} is attributed to stretching variation of P—O—P in polyphosphoric acid groups and the peak at 1470 cm^{-1} is attributed to C—H bending vibration of piperazine ring. The peak at 1640 cm^{-1} is assigned to N—H variable angle vibration of NH_2^+ and the peaks at 3010, 2780, 2600, 2230 cm^{-1} are attributed to N—H stretching variation of NH_2^+.

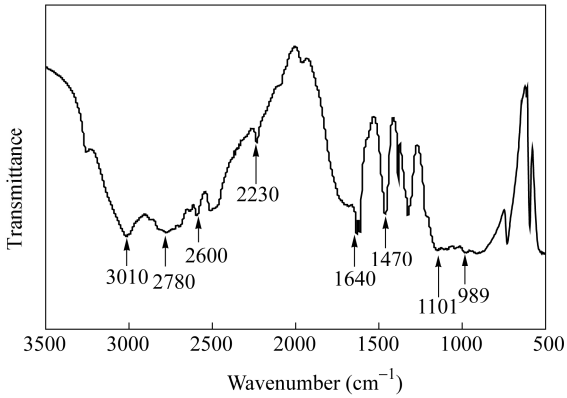

Fig. 1 FTIR spectrum of poly(phosphoric acid piperazine)

The ^{13}C- solid-state NMR spectrum of PPAP is shown in Fig. 2. A single resonance signal at 41.59 ppm is attributed to C in the piperazine ring. The ^{31}P solid-state NMR spectrum of PPAP is presented in Fig. 3, and the major peaks at −3.9 ppm to −7.5 ppm are attributed to P in the intermediate segment of PPAP molecular chain, and the relatively small peaks at 3.8 and 0.1 ppm are assigned to P in the terminal of PPAP structure. The characterization results of FTIR and NMR confirm the PPAP chemical structure.

Flame Retardancy of Cured Epoxy Resin

To evaluate the effect of synthesized PPAP on the flame retardancy for epoxy resin thermosets, LOI and vertical burning (UL-94) tests were conducted. The relevant data are summarized in Table 1. It can be seen that the pure epoxy resin thermosets burn continuously after ignited without dripping, and the LOI value is only 21.1%. However, the LOI value of cured EP/PPAP composites is dramatically increased

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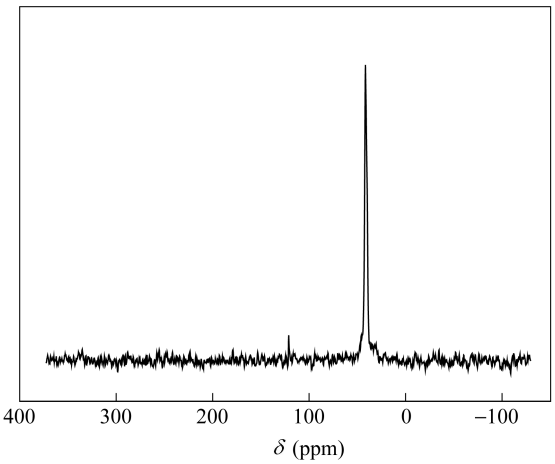

Fig. 2 ^{13}C solid-state NMR spectrum of PPAP

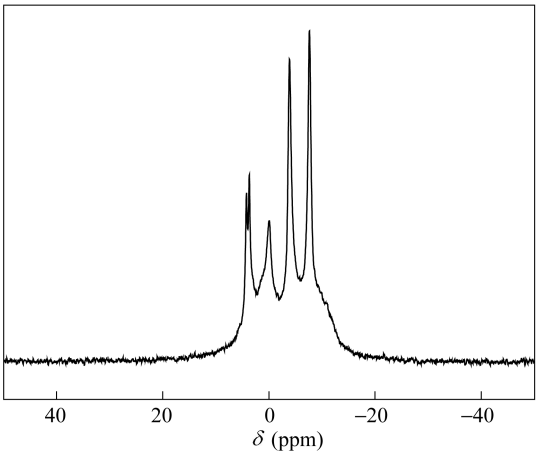

Fig. 3 ^{31}P solid-state NMR spectrum of PPAP

PPAP is only 1 wt%. The flame retardant performance of EP/PPAP thermosets is gradually enhanced with the increase of PPAP content in EP thermosets. The EP thermosets successfully pass the UL-94 V-0 flammability rating with the LOI value as high as 30.8% when the loading amount of PPAP is 5 wt%. All of the specimens have no droplets during UL-94 vertical burning tests. Gao *et al.*[36] synthesized the phosphorus-containing flame retardant trimer and incorporated it into EP thermosets. They doped about 20 wt% trimer into EP and the modified EP got 30.2% of LOI and UL-94 V-0 flammability rating. In our previous work[32], the polymelamine tetramethylene phosphonium sulfate (PMTMPS) was synthesized and used as a flame retardant additive for EP thermosets, and the samples passed UL-94 V-0 flammability rating when the loading amount of PMTMPS was 11 wt%. These facts mainly resulted from the relatively low phosphorus content in the prepared flame retardant additives. Compared with the phosphorus containing compounds reported previously[36, 37] and the phosphorus-nitrogen compounds[32] for flame retardant epoxy resin thermosets, the prepared PPAPs in this work possess higher flame retardant efficiency for epoxy resin thermosets. We speculate that the PPAP flame retardant additive in epoxy resin can act as the acid precursors that decompose to phosphoric and polyphosphoric acid during combustion. Such a function exerts the catalytic effect for epoxy resin thermosets and stimulates the formation of char layer[38]. Meanwhile the piperazine structure with excellent charring ability existing in PPAP also promotes inherent char-forming by the degradation of PPAP itself during combustion in the condensed phase. The formed char layer can stop the propagation of heat and oxygen to underlying polymer matrix during combustion and protect the underlying materials from further burning. On the other hand, the action of PPAP compound can enter into the vapor phase, in which PO, P and P2 species are produced and likely to react with H and OH radicals to form HPO during combustion[26, 27]. The reaction may interrupt the exothermic processes and suppress the combustion by a radical mechanism. Moreover, the piperazine groups in thermosets can release noncombustible gases, such as N_2 and NH_3 during combustion process, which dilute the flammable gases and reduce the oxygen concentration around the material. As a result, PPAP exerts flame retardant effect on gaseous and condensed phases simultaneously, thus PPAP additive presents superior flame retardant efficiency for EP thermosets.

Thermal Analysis of PPAP and Cured Epoxy Resin

We used thermal gravimetric analysis (TGA) to measure the weight loss of samples with increase of temperature, which provided direct information about the thermal stability, char formation and degradation behavior of the samples. The initial decomposition temperature ($T_{initial}$) is defined as the temperature at which the sample lost 1 wt% weight, T_{peak} is defined as the temperature of maximum weight loss rate, and R_{peak} is defined as the weight loss rate at which the sample experienced the maximum weight loss rate. The TGA and DTG curves of PPAP, cured pure EP and EP/5 wt% PPAP thermosets defined as flame retardant EP are shown in Fig. 4. The relevant thermal degradation data are summarized in Table 2. The flame retardant additive of PPAP started to decompose at 262.1 °C, and the char residue was 16.4 wt% at 800 °C, which revealed that the synthesized PPAP possessed excellent thermal stability and superior charring ability at high temperature. From the DTG curves shown in Fig. 4(b), it is seen that the whole degradation process of PPAP can be divided into three stages. The first step occurred from 278.2 °C to 328.1 °C and the peak centered at 305.7 °C, which could be attributed to the release of water due to a large number of P—OH groups in PPAP molecular structure. The second step appeared from 346 °C to 464 °C and peaked at 406.9 °C, and the weight loss at this stage was attributed to the decomposition and char-forming of PPAP. The third stage was from 473 °C to 634 °C due to the further decomposition of formed char layer. The pure EP thermosets decomposed at 326.9 °C and the char yield was only 14.4 wt% at 800 °C. As shown in Fig. 4(b), the thermal degradation of pure EP thermosets presented only one peak at 379.2 °C with the weight loss rate of 14.79%·min^{-1} due to the decomposition and char-forming of epoxy resin thermosets. The curves of EP/5 wt% PPAP thermosets are the result calculated from the curves of pure EP and PPAP in Fig. 4 based on their percentage in the thermosets. However, the initial thermal decomposition temperature of EP/5 wt% PPAP thermosets greatly decreased to 295.1 °C (326.9 °C for pure EP and

Table 2 Thermal degradation data of PPAP and cured epoxy resin composites

Sample	$T_{initial}$ (°C)	R_{1peak}/T_{1peak} (%·min^{-1}/°C)	R_{2peak}/T_{2peak} (%·min^{-1}/°C)	R_{3peak}/T_{3peak} (%·min^{-1}/°C)	Char residue at 800 °C (wt%)
PPAP	262.1	1.40/305.7	3.47/402.9	5.68/578.4	16.4
Pure EP	326.9	14.79/379.2	–	–	14.4
EP/5 wt% PPAP	295.1	11.64/356.6	–	–	21.0
EP/5 wt% PPAP (calculation)	324.6	14.15/379.3	–	–	14.5

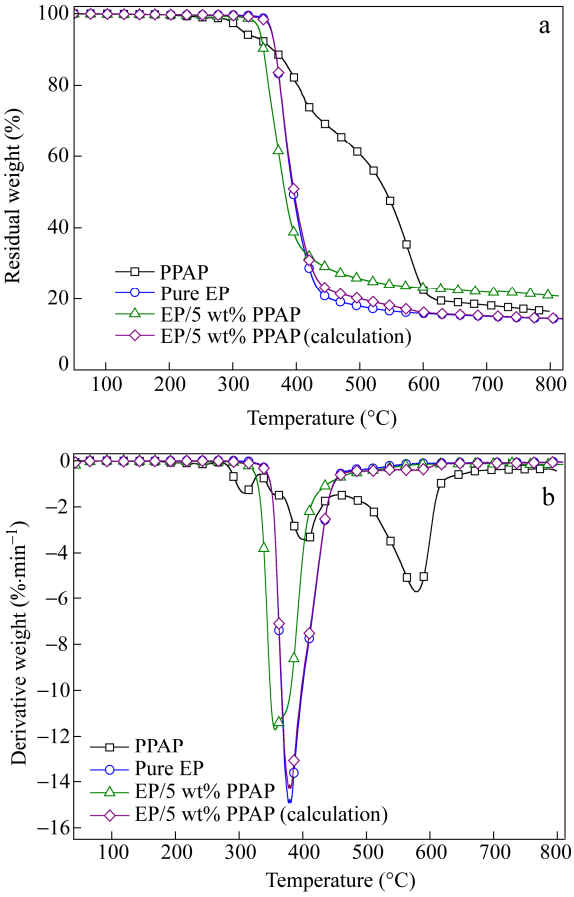

Fig. 4 (a) TGA and (b) DTG curves of PPAP and cured epoxy resin composites

324.6 °C for the calculated value of EP/5 wt% PPAP thermosets) due to the incorporation of PPAP into epoxy resin. The whole degradation course of EP/5 wt% PPAP only has one step ranging from 320 °C to 410 °C, and peaked at 356.6 °C with the weight loss rate of 11.46%·min^{-1}. The peak appeared earlier, the maximum weight loss rate is lower than that of cured pure EP and EP/5 wt% PPAP thermosets (calculated value). This may be attributed to the fact that the phosphorus-containing flame retardant in EP thermosets firstly decomposes to form phosphoric and polyphosphoric acid which react with epoxy resin matrix, and the reaction stimulates the epoxy resin degradation to form the protective char layer at early stage on heating. Moreover, the char residue increases from 14.4 wt% for pure EP, 14.5 wt% for EP/5 wt% PPAP thermosets (calculated value) to 21.0 wt% for EP/5 wt% PPAP thermosets, which further demonstrates that PPAP reacts with EP matrix and promotes the char formation of EP thermosets. Generally, the higher char yield will benefit to the enhancement of flame retardant performance of EP thermosets and the thermal degradation results coincide with the flame retardancy tests discussed above.

TG-IR is usually used to analyze the gas products during the thermal degradation process. In order to gain a deeper understanding of the flame retardant effect, the TG-IR spectra of pure EP and EP/5 wt% PPAP thermosets are detected. Their FTIR spectra of pyrolysis products after different degradation periods are shown in Fig. 5. It can be observed that there are characteristic bands of water (3654 cm^{-1}), carbon dioxide (2354 cm^{-1}) and compounds containing aromatic ring (1612, 1508 cm^{-1}) in the spectra of cured pure EP and EP/5 wt% PPAP, and the characteristic bands are almost similar between the two samples. Moreover, it was also found that EP/5 wt% PPAP thermoset released gas products at 33 min with the temperature of 310 °C, while the cured pure EP started to produce gas products at 35 min with the temperature of 330 °C, which was consistent with the results of TGA discussed above. It can be deduced that the introduction of PPAP stimulates the EP thermosets to decompose at early time and low temperature as compared with the cured pure EP.

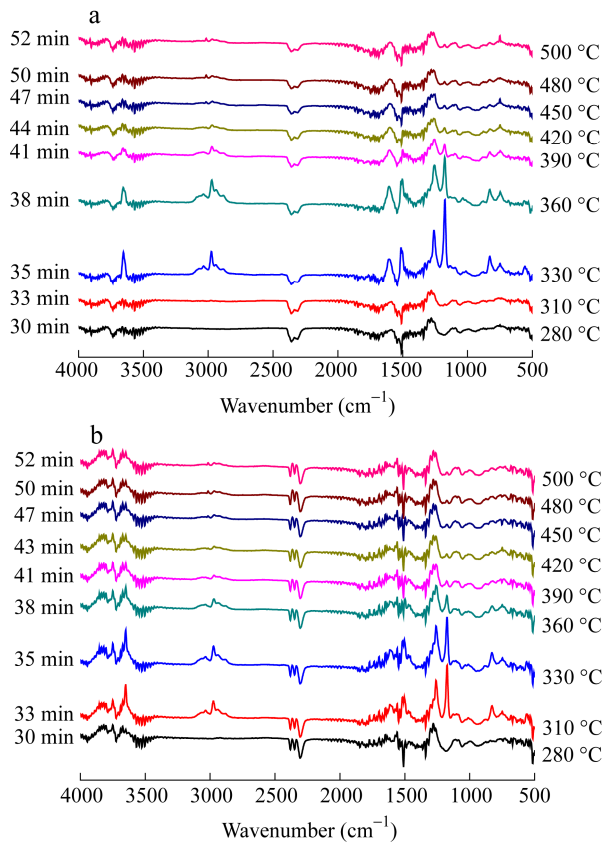

Fig. 5 FTIR spectra of volatile products from (a) cured pure EP and (b) EP/5 wt% PPAP at different temperatures

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Flammability Behavior of Cured Epoxy Resin

The cone calorimeter test has been widely used to evaluate the combustion performance of polymeric materials based on the oxygen consumption principle, and the results have good correlation with real fire disaster. The parameters, including time to ignition (TTI), heat release rate (HRR), peak heat release rate (PHRR), total heat release (THR), smoke produce rate (SPR), total smoke produce (TSP) and residual mass (RM) are measured, which are used to investigate the effect of PPAP on the combustion behavior of epoxy resin thermosets in real fires. Figures 6–8 and Table 3 present the plots and the detailed information of combustion behavior of pure EP and EP/5 wt% PPAP thermosets obtained from the cone calorimeter test at a heat flux of 50 kW·m^{-2}.

TTI is used to determine the influence of a flame retardant on ignitability. As shown in Table 3, TTI of EP/5 wt% PPAP thermosets decreases to 38 s (pure EP 63 s). This phenomenon may be due to the fact that there are many acid hydroxyl groups in PPAP structure (Scheme 1), and PPAP not only decomposes ahead of time itself but also promotes the epoxy resin matrix to degrade at the initial stage of heating,

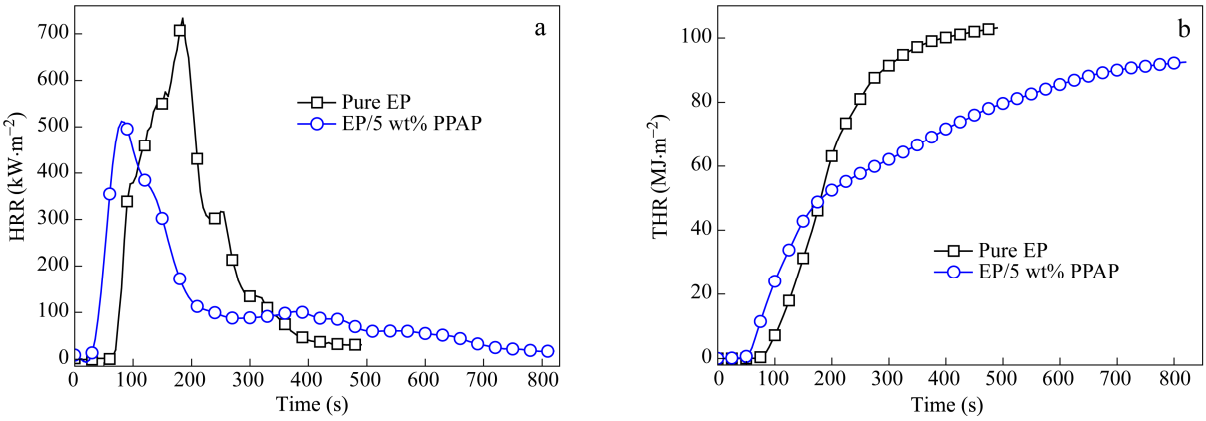

Fig. 6 (a) HRR and (b) THR curves of the cured pure EP and EP/5 wt% PPAP composites

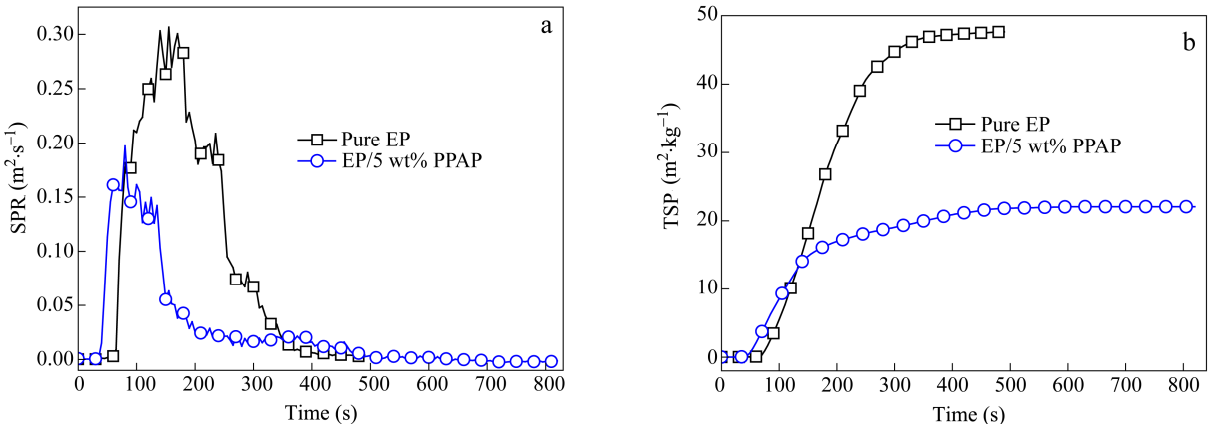

Fig. 7 (a) SPR and (b) TSP curves of cured pure EP and EP/5 wt% PPAP composites

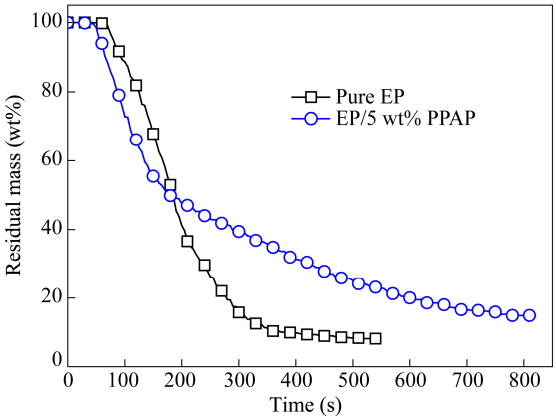

Fig. 8 Residual mass curves of the cured pure EP and EP/5 wt% PPAP composites

Table 3 Cone calorimeter data for the cured epoxy resin

Properties	Pure EP	EP/5 wt% PPAP
TTI (s)	63 ± 3	38 ± 2
Peak$_1$-HRR (kW·m^{-2})	731.2 ± 16.3	511.9 ± 11.2
$t_{Peak1\text{-}HRR}$ (s)	184 ± 3	80 ± 2
Peak$_2$-HRR (kW·m^{-2})	320.1 ±9.4	101.4 ±6.1
$t_{Peak2\text{-}HRR}$ (s)	253 ± 7	380 ± 9
THR (MJ·m^{-2})	103.2 ± 9.1	92.5 ± 7.5
Peak$_1$-SPR (m^2·s^{-1})	0.31 ± 0.03	0.19 ± 0.02
$t_{Peak1\text{-}SPR}$ (s)	155 ± 10	80 ± 6
Peak$_2$-SPR (m^2·s^{-1})	0.21 ± 0.02	0.02 ± 0.01
$t_{Peak2\text{-}SPR}$ (s)	235 ± 13	375 ± 11
TSP (m^2·kg^{-1})	47.6 ± 4.3	22.1 ± 3.1
Char residue (%)	8.1 ± 0.9	14.9 ± 1.1

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which is in accordance with the $T_{initial}$ results discussed above. It can be deduced that the catalytic decomposition effect of PPAP weakens the resistance of epoxy resin thermosets to ignition. In certain conditions, the degradation behavior ahead of time contributes to earlier charring during combustion and benefits to the better flame retardancy for EP thermosets.

HRR is recognized to be the most important parameter to quantify the size of fire. An effective flame retardant system normally shows a lower HRR value. Figure 6(a) shows the HRR curves of pure EP and EP/5 wt% PPAP thermoset. The results reveal that the cured pure EP burns rapidly after ignition and two HRR peaks appear during combustion process. The first HRR peak appears at 184 s with a PHRR of 731.2 $kW \cdot m^{-2}$, corresponding to the combustion of epoxy resin thermosets. The second HRR peak can be observed at 253 s with a PHRR of 320.3 $kW \cdot m^{-2}$, which mainly results from the crack of formed char layer with poor strength and thermal stability. As shown in Fig. 6(a), the HRR curve of EP/5 wt% PPAP thermosets also displays two peaks, but the peaks appear earlier than that of pure EP. The first HRR peak of EP/5 wt% PPAP thermosets appears at 80 s with a PHRR of 511.9 $kW \cdot m^{-2}$. It is attributed to the decomposition product of PPAP, which promotes EP matrix charring ahead of time. Meanwhile, the PPAP itself with piperazine structure is also charring during combustion, and the formed char layer on material's surface efficiently prevents the transfer of heating from the samples during the combustion process, thus degrading the intensity of combustion pyrolysis reactions. The second HRR peak of EP/5 wt% PPAP thermosets is not obvious and appears at 380 s with a low PHRR value of 101.4 $kW \cdot m^{-2}$, which is corresponding to the formed char layer with relatively high strength at high temperature. Consequently, the THR of EP/5 wt% PPAP decreased to 92.5 $MJ \cdot m^{-2}$. Compared with pure EP (103.2 $MJ \cdot m^{-2}$), it decreased 10.4% by the incorporation of 5 wt% PPAP into EP thermosets (Fig. 6b and Table 3).

Smoke in a real fire means more risk of suffocation, even more fatal than heat release. The SPR and TSP curves of pure EP and EP/5 wt% PPAP thermosets are presented in Fig. 7. It can be seen that the tendency of SPR curves is similar to the HRR curves (Fig. 7a), and the SPR curve of pure EP presents two peaks. The first peak appears at 155 s with the value of 0.31 $m^2 \cdot s^{-1}$ due to the combustion of EP thermosets, and the second peak appears at 235 s with the value of 0.21 $m^2 \cdot s^{-1}$, corresponding to the further combustion of pure EP thermosets caused by the crack of formed char layer. Similar to the HRR curve, the peaks of SPR curve of EP/5 wt% PPAP appear ahead of time than that of pure EP, which is corresponding to the rapid decomposition of PPAP at the initial stage on heating and the release of NH_3 and H_2O. Meanwhile, the decomposition products of PPAP can stimulate the degradation of EP matrix and charring, resulting in the smoke emission ahead of time. However, the values of SPR for EP/5 wt% PPAP thermosets are evidently lower than that of pure EP, as shown in Fig. 7(a). This is due to the formation of compact, continuous char layer with high strength and thermal stability on the surface of materials, which effectively prevents the transfer of heat and restricts the production of combustible gases, thus suppresses the intensity of combustion pyrolysis reactions and decreases the release of quantity of smoke. Moreover, as shown in Fig. 7(b) and Table 3, the TSP value of EP/5 wt% PPAP thermosets greatly decreases to 22.1 $m^2 \cdot kg^{-1}$. Compared with cured pure EP (47.6 $m^2 \cdot kg^{-1}$), it decreases by 53.6%.

Figure 8 gives the RM curves versus time for the pure EP and EP/5 wt% PPAP thermosets. RM is recognized to be the primary parameter responsible for decreasing the HRR and SPR of a material during combustion. It can be seen that the cured pure EP loses its weight fast and leaves 8.1 wt% residual char at the end of combustion, while the char residue for EP/5 wt% PPAP thermosets is enhanced to 14.9 wt% due to the introduction of 5 wt% PPAP into EP thermosets. This result further demonstrates that PPAP stimulates the EP matrix charring during combustion and the formed char layer protects the undying matrix from further degradation, which leads to the incomplete decomposition of epoxy resin thermosets and increases the char residue at the end of combustion.

Morphologies of Char Residue

In order to further investigate the relationship between the morphology of char layers and flame retardant properties of the cured EP composites, the char residues of cured pure EP and EP/5 wt% PPAP after cone calorimeter tests were measured by digital cameral and SEM magnified by 3000 times (Figs. 9 and 10). As shown in Fig. 9(a), the pure EP is nearly burnt out and presents a fragmentary structure with a small amount of residual char, which is unable to serve as a protective layer and exert barrier effect. However, the EP/5 wt% PPAP sample shows continuous, intumescent and compact char layer with integral structure due to the incorporation of PPAP, as shown in Fig. 9(b). This is conducive to serving as the isolated layer and reducing the exchange of heat and oxygen, and thus enhances the flame

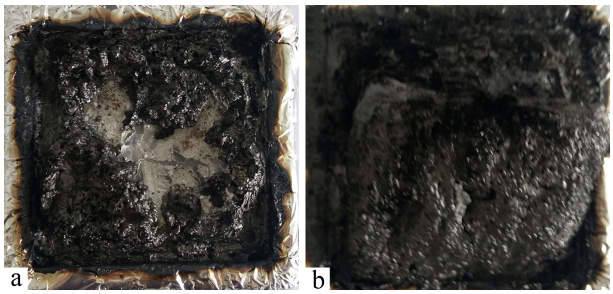

Fig. 9 The digital photos of the char residue after the cone calorimeter tests: (a) pure EP, (b) EP/5 wt% PPAP

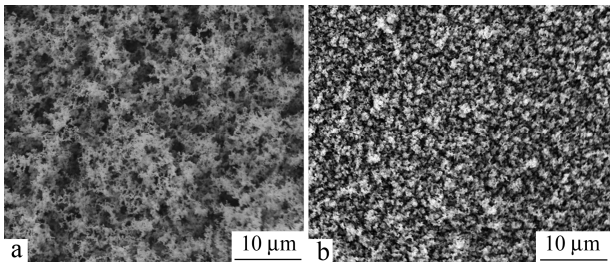

Fig. 10 SEM images of the char residue after cone calorimeter tests: (a) pure EP, (b) EP/5 wt% PPAP

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retardant performance of the sample. Moreover, it can be seen that the surface morphology of char layer for cured pure EP presents a relatively loose structure, including some small crevasses and holes on the surface due to insufficient char formation during combustion (Fig. 10a). Therefore, heat and flammable volatiles could penetrate the char layer into the flame zone and lead to poor flame retardancy for pure EP thermosets. On the contrary, the char layer for cured EP/5 wt% PPAP is more homogenous and compact than that of the cured pure EP, as shown in Fig. 10(b). The results suggest that the introduction of PPAP into EP thermosets not only stimulates EP matrix to form char layer but also promotes inherent char-forming by the degradation of PPAP itself during combustion, resulting in a more sufficient and compact char layer. Consequently, the formed char layer effectively inhibits the transformation of heat and oxygen into the interior matrix and flammable volatiles into flame zone, suppressing the further degradation and combustion of EP matrix and resulting in superior flame retardancy of EP/5 wt% PPAP thermosets.

Chemical Compositions of Char Residue

In order to further explore the degradation behavior and flame retardant mechanism of the cured EP/PPAP composites, the char residues of pure EP and EP/5 wt% PPAP thermosets after cone calorimeter tests were measured by FTIR. The relevant spectra are depicted in Fig. 11. For pure EP (curve (a) of Fig. 11), the characteristic absorption peaks are: 2966 and 2864 cm^{-1} (C—H), 1610 and 1512 cm^{-1} (aromatic ring) caused by the decomposition and charring of pure EP thermosets. Compared with curve (a), some additional absorption peaks appear in curve (b) for the char residue of EP/5 wt% PPAP thermosets. The characteristic absorption peaks at 1112, 1040 and 943 cm^{-1} indicate the formation of P—O—P and P—O—C structures[39]. The results demonstrate that the phosphorus in PPAP is decomposed under heating with sufficient oxygen, leading to the phosphorus containing oxides in the residual char, which can stimulate the formation of sufficient char residue and enhance the flame retardancy of EP/5 wt% PPAP thermosets.

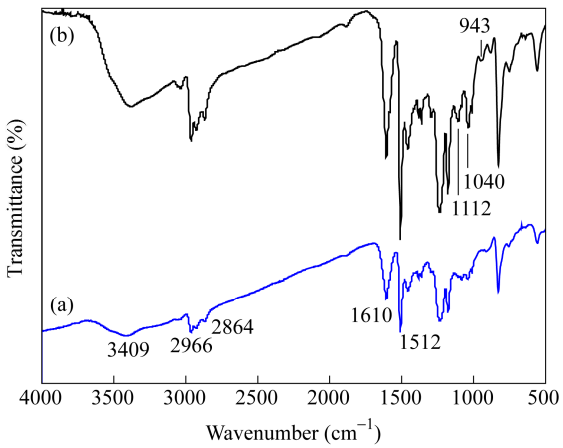

Fig. 11 FTIR spectra of the char residue: (a) pure EP, (b) EP/5 wt% PPAP

The chemical compositions of residual char surface for pure EP and EP/5 wt% PPAP thermosets after cone calorimeter tests were analyzed by XPS measurement. The relevant data are listed in Table 4. It can be observed that the flame retardant elements of phosphorus are detected in the char residue surface for EP/5 wt% PPAP thermosets with the relative content of 2.80% and the relative content of oxygen is higher than that of cured pure EP. Combined with the results of FTIR for char residues, such a change is due to the fact that the phosphorus in thermosets is decomposed and oxidized under heating and sufficient oxygen, leaving the phosphorus containing oxides with high thermal-oxidative stability in the char layer. As a result, the formed char layer with high quality protects the underlying substance from further oxidation and decomposition, resulting in the high char yield and superior flame retardancy for EP thermosets during combustion.

Table 4 Element relative content of the char layer for cured epoxy resin by XPS analysis

Element	Pure EP		EP/5 wt% PPAP	
	Peak BE (eV)	Atomic percentage (%)	Peak BE (eV)	Atomic percentage (%)
C	284.60	84.24	284.22	74.62
N	399.32	3.93	398.62	5.89
O	532.96	11.83	531.62	16.69
P	134.00	–	133.44	2.80

Mechanical Properties of Cured Epoxy Resin

The mechanical properties of pure EP and EP/PPAP thermosets with different contents of PPAP additive are presented in Table 5. The tensile and flexural strength values of pure EP thermosets are 57.2 and 102.3 MPa, respectively. The tensile and flexural strength values of cured EP/PPAP composites gradually decrease with increasing the content of PPAP in EP thermosets. The tensile and flexural strength for EP/5 wt% PPAP thermosets are 44.7 and 85.2 MPa, which are decreased by 21.9% and 16.7%, respectively. This phenomenon may be attributed to that the incorporation of PPAP flame retardant additive hinders the formation of crosslinking network of epoxy resin thermosets. On the other hand, the thermosets decompose to a certain degree due to the presence of a number of acid hydroxyl groups in PPAP.

Table 5 Mechanical properties of cured pure EP and EP/PPAP composites

Sample	Tensile strength (MPa)	Flexural strength (MPa)
EP-0	57.2 ± 2.2	102.3 ± 4.3
EP-1	52.6 ± 2.1	98.4 ± 4.1
EP-2	50.8 ± 1.3	94.9 ± 3.2
EP-3	48.1 ± 1.8	91.6 ± 4.4
EP-4	46.4 ± 1.1	87.1 ± 3.4
EP-5	44.7 ± 1.2	85.2 ± 3.6
EP-6	43.4 ± 1.6	81.8 ± 3.8

CONCLUSIONS

A phosphorus-nitrogen containing flame retardant additive of poly(phosphoric acid piperazine) (PPAP) was successfully synthesized, and used as an additive for flame retardant epoxy resin thermosets. The obtained PPAP presents high flame

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retardant efficiency for EP matrix. EP/5 wt% PPAP thermosets can pass UL-94 V-0 flammability rating and its LOI value is as high as 30.8%. The incorporation of PPAP stimulates the decomposition of epoxy resin matrix at earlier process of heating due to the catalytic decomposition effect, which promotes the release of noncombustible gas and benefits to the formation of sufficient, continuous and phosphorus containing char layer with high thermal-oxidative stability. The formed char layer efficiently prevents the underlying materials from further combustion and enhances the fire retardant performance, consequently resulting in the reduction of HRR, THR, SPR, TSP and so on. It can be inferred that PPAP is an efficient charring agent for epoxy resin and it exerts flame retardant effect in condensed and gaseous phases simultaneously. As a result, PPAP endows the epoxy resin matrix with superior flame retardant efficiency.

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